Living/Controlled Anionic Polymerization and Copolymerization of Epichlorohydrin with Tetraoctylammonium Bromide−Triisobutylaluminum Initiating Systems

Stéphane Carlotti,* Amélie Labbé, Virginie Rejsek, Stéphane Doutaz, Matthieu Gervais, and Alain Deffieux*

Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, UMR 5629, CNRS−ENSCPB, 16 avenue Pey Berland, 33607 Pessac Cedex, France

Received June 25, 2008; Revised Manuscript Received July 30, 2008

ABSTRACT: A weakly nucleophilic initiating system obtained by the combination of triisobutylaluminum and tetraoctylammonium bromide has been successfully used to achieve the controlled polymerization of epichlorohydrin (ECH) in hydrocarbon at temperatures ranging from −30 °C to room temperature. Besides the formation of a 1:1 aluminate complex of low nucleophilicity between the aluminum derivative and the tetraalkylammonium salt, the strategy consists of the formation of a strongly activating complex between the Lewis acid and the epoxide monomer. To that aim trialkylaluminum is added in slight excess with respect to the tetraalkylammonium salt ($[i\text{-Bu}_3\text{Al}]/[\text{NOct}_4\text{Br}] > 1$). In these conditions the reactivity of ECH toward nucleophiles is strongly enhanced and the ring opening polymerization proceeds in the presence of weak nucleophiles leading to nonreacted chloromethyl function of the epichlorohydrin. This contrasts with conventional anionic polymerization, which requires much stronger nucleophiles for the ring opening. Fast and controlled polymerization of ECH up to high molar masses and the synthesis of random and block copolymers with propylene oxide were readily achieved.

Introduction

Polyepichlorohydrin (poly(ECH)) and ECH copolymers with oxirane monomers constitute a class of functional polymeric materials with specific characteristics of interest for applications in various domains.

High molar mass poly(ECH)s were first prepared by Vandenberg[1] through a cationic coordination mechanism in presence of organometallic catalysts. These rubbery polymers ($T_g = -22$ °C) exhibit elastomeric properties associated with a very good resistance to oil, ozone and thermal aging. This combination of properties makes them particularly useful in automotive applications, in particular in engine compartments. Commercially important products belonging to this family[2] are poly(ECH), ECH-ethylene oxide (EO) copolymers and ECH−EO−allyl glycidyl ether (AGE) terpolymers, which are sulfur vulcanizable rubbers. Poly(ECH) and ECH−EO copolymers found also applications as flexible solid electrolytes for the storage of energy[3–7] as well as reactive polymer backbone for the synthesis of various functional polyethers[8,9] such as, for example, the preparation of poly(azido glycidyl ether) (PAG) used as energetic binder for solid propellants.[10,11]

The ring-opening polymerization (ROP) of ECH has been studied for many years.[12–14] Due to a predominant reaction between chloromethyl group of the monomer and the highly nucleophilic propagating species used in conventional anionic polymerization of epoxides this approach is prohibited. Therefore the different synthetic strategies developed up to now are mainly based on cationic mechanisms or on coordinated polymerization processes.

They are two different mechanisms by which cationic ROP of ECH can proceed (Scheme 1): the activated chain end mechanism (ACE) in which the active propagating center is an oxonium ion located at the chain end while the monomer is neutral, and the monomer activated mechanism (AM) where the monomer forms an ionic complex with a protonic species (a Brönsted acid) while the chain end is a neutral hydroxyl. The use of protonic acids, stable organic salts and Lewis acids in combination with a small proportion of protogenic species (often water) as initiating systems yields an ACE type mechanism, which leads the formation of a mixture of ill-defined linear and cyclic poly(ECH) oligomers. This is due to the contribution of important side reactions involving propagating species and the oxygen of the poly(ECH) chains that yield chain transfer, backbiting and termination during the propagation.[15] In the AM cationic polymerization of ECH, which takes place at low instantaneous ECH concentration and in the presence of low molar mass diols as chain initiator, the formation of the cyclic oligomer fraction is strongly suppressed, thus allowing the preparation of dihydroxytelechelic poly(ECH), useful as polyurethane precursors. The AM cationic process remains limited however to the synthesis of low molar mass poly(ECH) (<2500 g/mol).[15]

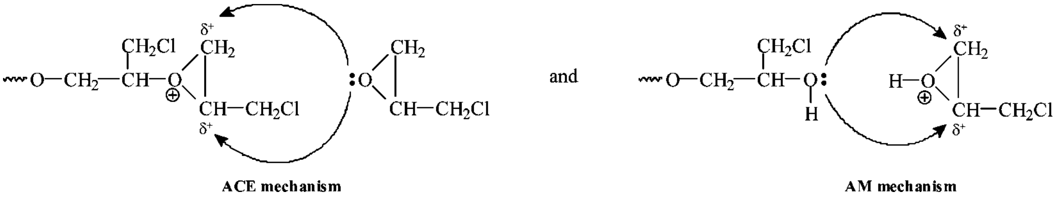
The strategy for the synthesis of high molar mass poly(ECH) consists of the use of coordination catalysts derived from the monometallic trialkylaluminum/H_2O/acetylacetonate systems of Vandenberg.[1,16,17] The proposed polymerization mechanism shown in Scheme 2 involves the activation of the monomer by an aluminum species. The attack of the activated monomer by adjacent poly(ECH)-OAl chain then proceeds. Hsieh has shown that the combination of trialkylaluminum with zinc acetylacetonate and water could also polymerize epichlorohydrin up to high molar masses.[18] At about the same time, catalytic systems based on the combination of dialkylaluminum acetylacetonate (R_2AlAcac), water and diethylzinc were able to give high molar masses poly(ECH).[19] The bimetallic nature of these systems was considered as the main factor for the observed high activity. A bimetallic species containing aluminum and zinc atoms (Zn−O−Al) was proposed as the active polymerization site, zinc atoms acting as monomer coordination centers and aluminum as chain growing site. The use of acetylacetonate derivatives of rare earth metals in association with trialkylaluminum[20] as well as complex quaternary catalytic systems associating trialkylaluminum, phosphoric acid, an aromatic amine and water[21] revealed high activities for the synthesis of

---

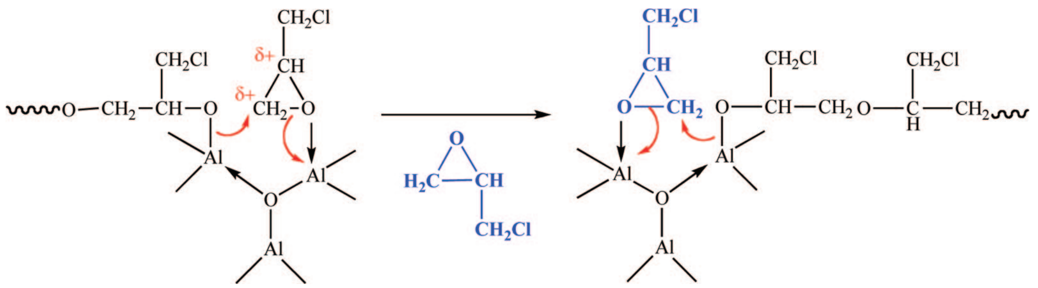
* Authors to whom correspondence should be addressed. E-mail: carlotti@enscpb.fr; deffieux@enscpb.fr.

10.1021/ma801422c CCC: $40.75

Scheme 1



Scheme 2. Vandenberg Mechanism Adapted for the Polymerization of ECH



poly(ECH). These systems opened the field of epichlorohydrin-based copolymers with some limitations concerning the molar masses, conversions or dispersities when high masses were expected.[21–27]

We have shown recently that the association of trialkylaluminum with initiators such as alkali metal or tetraalkylammonium salts, at [AlR_3]/[initiator] ratios higher than one, constitutes very efficient initiating systems for the living/controlled anionic polymerization of propylene oxide and ethylene oxide[28–30] through strong monomer activation. In this article we have extended this approach to ECH, a chloromethyl functional oxirane for which polymerizations based on strongly nucleophilic active species, typically operating in conventional anionic ring opening polymerization, are prohibited. The polymerization of ECH using tetraalkylammonium bromide, in association with triisobutylaluminum, as well as its random and block copolymerization with propylene oxide is investigated.

Experimental Section

Materials. Epichlorohydrin (ECH, 99%, Aldrich) and propylene oxide (POx, 99%, Fluka) were purified over CaH_2, distilled under vacuum and stored for 15 min in a glass flask equipped with PTFE stopcocks in the presence of triisobutylaluminum to remove traces of impurities. Both were finally distilled under vacuum and stored under vacuum at RT in graduated glass tubes until use. Triisobutylaluminum (i-Bu_3Al) (1 mol/L in toluene, Aldrich) was used without further purification. Toluene (98%, J.T. Baker) was purified with polystyryllithium seeds, distilled under vacuum and stored in graduated glass tubes. Tetraoctylammonium bromide ($NOct_4Br$, 98%, Aldrich) was dried under vacuum and then solubilized into dried toluene followed again by a complete drying under dynamic vacuum. Tetraalkylammonium salt solutions of known concentration were then prepared in dried toluene and stored in graduated glass tubes fitted with PTFE stopcocks.

Procedures. All (co)polymerizations were performed between −30 and 25 °C under argon in a high pressure glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks. The reactor was flamed under vacuum and cooled down prior introduction of solvent and monomer(s) through connected glass tubes. Then a toluene solution of initiator and finally the trialkylaluminum catalyst were added *via* a syringe under argon. For the block copolymerizations, the second monomer was introduced after the desired reaction time. A small amount of ethanol was then added to stop the reaction. Polymer conversions were determined gravimetrically after complete drying of the polymer under vacuum, at 50 °C.

Kinetic studies were followed by dilatometry measurements which were performed in a glass dilatometer previously flamed. The initiator solution was first added using a syringe, and the system was thermostatted at the desired temperature. Then the solvent, the monomer and finally triisobutylaluminum were successively added. Monitoring of the reaction was immediately followed by recording the volume level of the solution in the capillary tube attached to the reactor.

Table 1. Polymerization of Epichlorohydrin Initiated by $NOct_4Br/i\text{-}Bu_3Al$ (Toluene, 20 °C[a], [ECH] = 3 M)

run no.	[Al]/[$NOct_4Br$]	time (h)	conversion %	$\bar{M}_n$ (theor)[b] (g/mol)	$\bar{M}_n$ exptl (g/mol)	$\bar{M}_w/\bar{M}_n$
1	0[c]	24	0			
2	1.0	24	0			
3	1.5	2.3	100	10 000	9 400	1.14
4	1.5	2.0	100	20 000	20 200	1.17
5	2.6	2.5	100	30 000	30 200	1.11
6	1.5	24	50	25 000	20 800	1.08
7	2.7	7.2	100	47 500	44 300	1.12
8	2.7	6.0	100	50 000	52 000	1.13
9	5.4	8.0	100	100 000	83 500	1.23

[a] Initiation of the polymerization was performed at −30 °C and the temperature of the system let to increase to 20 °C. [b] calculated at final conversion. [c] Experiment performed with $NOct_4Br$ in absence of trialkylaluminum.

Analysis. Polymer and copolymer molar masses were determined by SEC at 20 °C using THF as eluant on a Jasco apparatus equipped with a Varian 2510 HPLC-pump, a refractive index Jasco detector and fitted with four TSK gels HXL columns (2000, 3000, 4000 and 5000), at an elution rate of 0.8 mL/min. Polystyrenes were used as standards.

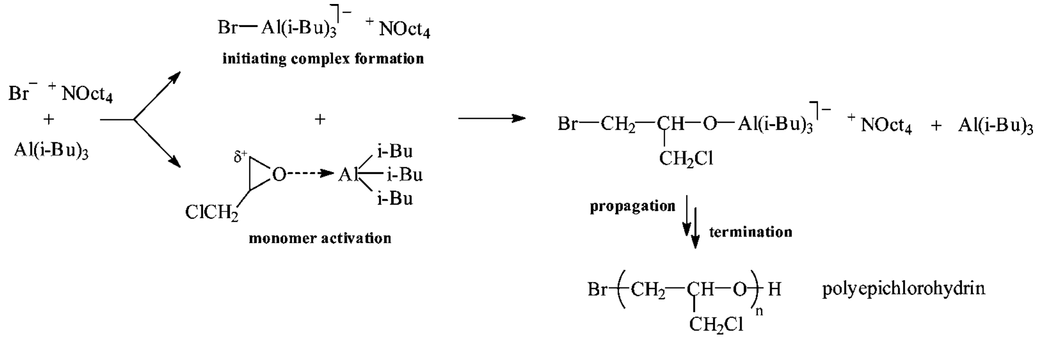
^1H (400 MHz) NMR measurements of PPOx-*co*-PECH were performed on a Brüker Avance 400 spectrometer, in $CDCl_3$ at room temperature.

Results and Discussion

The polymerization of epichlorohydrin has been investigated in toluene using tetraoctylammonium bromide as initiator and triisobutylaluminum as activator. At 20 °C, depending on the amount of trialkylaluminum additive, a very fast ECH polymerization takes place in the first minutes of reaction. In order to lower the initial reactivity the polymerization was started at −30 °C and then the temperature of the system was allowed to rise up to room temperature. As it may be seen in Table 1, in most cases, complete ECH conversion is reached in few hours in these conditions, even when high molar masses are targeted.

Similarly to what was previously observed for propylene oxide and ethylene oxide,[29,30] the polymerization of ECH

Scheme 3



initiated by tetraoctylammonium bromide readily takes place in the presence of a slight excess of Lewis acid with respect to the initiator. As shown in Table 1, no polymerization occurs (run 2) at a ratio [Al]/[$NOct_4Br$] equal to 1 whereas 100% conversion is achieved in 2.3 h, for 1.5 equiv of *i*-Bu_3Al with respect to the initiator, yielding a poly(ECH) of about 10 000 g/mol. In about the same polymerization time, quantitative formation of a poly(ECH) of 30 000 g/mol is achieved with a ratio [Al]/[$NOct_4Br$] equal to 2.6, thanks to the higher concentration of *i*-Bu_3Al. This is consistent with a reaction mechanism involving the formation of a $NOct_4Br$:triisobutylaluminum (1:1) aluminate complex, a strong ECH activation by the alkylaluminum in excess and attack of the activated ECH by the aluminate complex (Scheme 3).

In all the experiments the chain dispersity is narrow and a good agreement is observed between theoretical poly(ECH) molar masses, calculated assuming the formation of one chain per tetraoctylammonium bromide, and experimental values. The evolution of poly(ECH) number-average molar mass with monomer conversion is shown in Figure 1 for a typical experiment. It reveals a linear increase of the molar masses with ECH conversion in direct relation with the equation $\bar{M}_n = M_0[\mathrm{ECH}]_{\mathrm{consumed}}/[\mathrm{NOct_4Br}]$. Narrow distributions, full conversions, linear increase of $\bar{M}_n$ vs conversion and our previous results on the controlled polymerization of propylene oxide with a similar initiating system[28–30] let us suppose that PS, used as SEC standards, and PECH hydrodynamic volumes should not be so different as far as experimental PECH molar masses are in the same range as calculated ones.

These results are consistent with a good control of the ECH polymerization and therefore a very selective epoxide ring opening reaction by the initiating and propagating aluminate species, without any noticeable reaction onto the chloromethyl group of the monomer, behavior in strong contrast with the conventional ECH anionic polymerization, which involves much more nucleophilic alkoxide active species.

A kinetic study of ECH consumption with time was performed at 0 °C by sampling the polymerization medium, Figure 2. Results indicate the presence of two relatively distinct polymerization periods. In the first stage, up to about 60% conversion, a fast ECH polymerization takes place, whereas an important slow down of the polymerization is observed at higher monomer conversions. The consequence is that for polymerization performed at low [AlR_3]/[NR_4Br] ratio, final ECH conversion can be incomplete when high molar mass poly(ECH) are targeted, run 6, Table 1. This was tentatively attributed to a decrease of the activated monomer concentration in the reaction medium, due to predominant complexation of trialkylaluminium by the oxygens of formed poly(ECH) chains at high monomer conversion. The addition of a higher initial amount of *i*-Bu_3Al allowed us to get high molar mass poly(ECH) and quantitative monomer conversion in relatively short reaction times as illustrated by runs 7 and 8, Table 1. Using a ratio [AlR_3]/[NR_4Br] of 5.4, a poly(ECH) with $\bar{M}_n$ = 83 000 g/mol (for a theoretical value of 100 000 g/mol) and a dispersity of 1.23 was obtained in 8 h at room temperature. The amount of triisobutylaluminum in this case remains quite low since it corresponds to a ratio [AlR_3]/[ECH] of less than 0.5% molar.

The initial ECH polymerization rate (R_p) at 0 °C was calculated in the first reaction stage from the slope of the monomer consumption versus time and compared with the one determined for propylene oxide (POx) in similar reaction conditions. Kinetics of the activated anionic epoxide polymerization can be expressed by the equation $R_p = k_p[\mathrm{NOct_4Br}]_0[\mathrm{M}^*]$

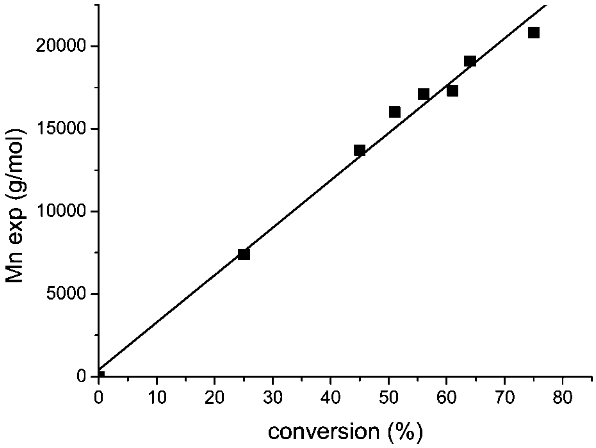


Figure 1. Variation of the number-average molar mass with ECH conversion in the epichlorohydrin polymerization initiated by $NOct_4Br$ in the presence of *i*-Bu_3Al (toluene, 0 °C, [Al]/[$NOct_4Br$] = 1.5 ([$NOct_4Br$] = 9.3×10^{-3} mol/L, [ECH] = 3 mol/L).

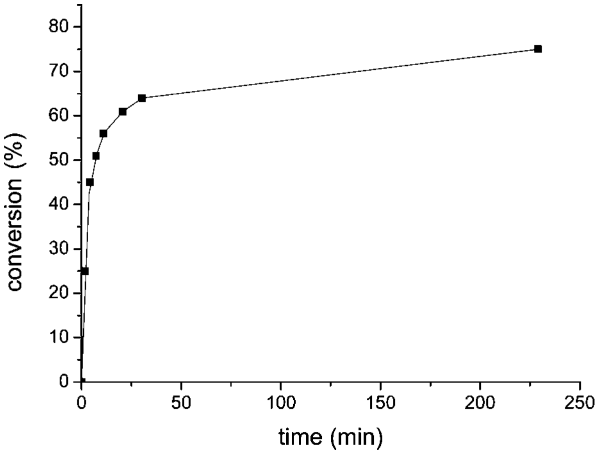


Figure 2. Conversion vs time plot for epichlorohydrin polymerization initiated by $NOct_4Br$ in the presence of *i*-Bu_3Al (toluene, 0 °C, [Al]/[$NOct_4Br$] = 1.5 ([$NOct_4Br$] = 9.3×10^{-3} mol/L, [ECH] = 3 mol/L).

Table 2. Polymerization Rate Constants of ECH and POx Initiated by NOct$_4$Br in Presence of Triisobutylaluminum (Toluene, $T = 0$°C, [NOct$_4$Br] = 9.25 10^{-3} mol/L, [Al]/[NOct$_4$Br] = 1.5, [Monomer] = 3 mol/L, $\bar{M}_n$ (theor) = 30 000 g/mol)

monomer	10^3[NOct$_4$Br]mol/L	[monomer]/ [NOct$_4$Br]	slope[a] of conv = $f(t)$	k_p[M*] (min^{-1})	k_p (L·mol^{-1}·min^{-1})
POx	5.81	526	3.5	1 800	650 000
ECH	9.46	316	10.5	3 300	700 000

[a] Calculated from 0 to 40 first percents of ECH conversion.

Table 3. Random Copolymerization of ECH and POx (Toluene, Time = 2 h, [Al]/[NOct$_4$Br] = 1.5, Conversion = 100%)

run	[POx]/[ECH]	[NOct$_4$Br] (mol/L)	[ECH + POx] (mol/L)	T (°C)	$\bar{M}_n$ (theor) (g/mol)	$\bar{M}_n$ (exp) (g/mol)	$\bar{M}_w/\bar{M}_n$
1	50/50	9.3×10^{-3}	1.4	20[a]	12 000	11 000	1.10
2	50/50	8.5×10^{-3}	2.5	20[a]	20 000	22 000	1.09
3	50/50	9.7×10^{-3}	2.1	20[a]	16 000	16 000	1.20
4	33/66[b]	9.9×10^{-3}	2.6	0	6 000	8 000	1.15

[a] Initiation was performed at −30 °C and the system allowed to increase. [b] Copolymerization carried out at 0 °C and stopped at 30% conversion.

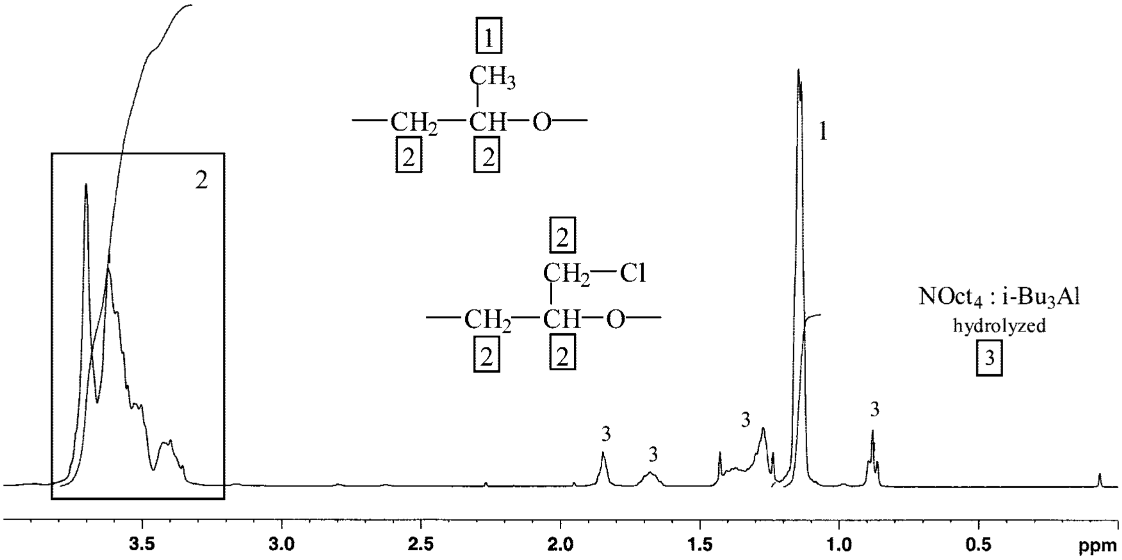


Figure 3. 400 MHz ^{1}H NMR spectrum of a random poly(POx)-*co*-poly(ECH) (run 4, Table 3) in CDCl$_3$.

where k_p is the propagation rate constant, and M* represents the trialkylaluminum activated monomer. [M*] was taken equal to $[\mathrm{Al}]_0 - [\mathrm{NOct_4Br}]_0$ since the first equivalent of *i*-Bu$_3$Al is considered to be quantitatively trapped in the 1:1 aluminate complex, as indicated by the absence of reactivity up to this stoichiometry (run 2, Table 1). The corresponding k_p[M*] values and k_p, which allow one to get rid of the influence of activator concentration, are collected in Table 2.

In the examined reaction conditions (toluene, $T = 0$ °C, [Al]/[NOct$_4$Br] = 1.5, [M] = 3 mol/L, the estimated k_p values are very close for the two monomers. The high rate constant observed for ECH, as well as for POx,[30] can be explained by a strong monomer activation resulting from its complexation with *i*-Bu$_3$Al. This yields fast ring-opening even in the case of the weakly nucleophilic aluminate complex which acts as propagating species. One major advantage of the monomer activation mechanism is the enhanced selectivity of the initiating and propagating species toward the ring-opening reaction. No noticeable contribution of transfer reactions or attack onto the chloromethyl group of ECH is observed, thanks to the low reactivity of the involved active species. The stereospecificity of monomer insertion was also studied by ^{13}C NMR (see Supporting Information). This polymerization system yields atactic PECH as for PPOx.[28]

The random and block copolymerization of ECH with POx was further investigated since these monomers present quite similar reactivity and can be polymerized in same experimental conditions. As shown in Table 3, random copolymers can be readily obtained in toluene using the NOct$_4$Br:*i*-Bu$_3$Al system at a ratio [Al]/[NOct$_4$Br] = 1.5. In these conditions copolymers with controlled molar masses and narrow dispersity could be obtained in less than two hours.

The ^{1}H NMR spectrum of copolymer 4, Table 3, recovered at partial comonomer conversion confirms the slightly faster incorporation of POx in the copolymer, Figure 3. Starting from a 33/66 POx/ECH molar comonomer composition, the copolymer possesses 48% of POx units and 52% of ECH units at 30% conversion.

In order to determine more precisely the POx/ECH comonomer reactivity ratios a series of copolymerization experiments using various initial comonomer compositions was performed in toluene at 0 °C (ratio [Al]/[NOct$_4$Br] = 1.5). Polymerizations were stopped at very low conversion (<10%), and the reactivity ratios were determined using the Kelen−Tüdos method:[31] The values obtained, $r_{\mathrm{POx}} = k_{\mathrm{POx-POx}}/k_{\mathrm{POx-ECH}} = 1.21$ and $r_{\mathrm{ECH}} = k_{\mathrm{ECH-ECH}}/k_{\mathrm{ECH-POx}} = 0.16$, are indicative of a slightly higher reactivity of POx compared to ECH monomer toward both POx and ECH aluminate propagating ends. These results are consistent with a random distribution of predominantly isolated ECH units and the formation of PPOx short sequences into the copolymer. For comparison, the only literature data available concerns POx/ECH copolymerization, by an anionic coordination mechanism,[21] in the presence of a quaternary catalytic system *i*-Bu$_3$Al−H$_3$PO$_4$−C$_6$H$_5$N(CH$_3$)$_2$−H$_2$O. Relatively close reactivity ratios $r_{\mathrm{POx}} = 2.75$ and $r_{\mathrm{ECH}} = 0.11$ were obtained.

On the grounds of the living/controlled character of the activated anionic polymerization of both POx and ECH, the synthesis of POx/ECH block copolymers by sequential monomer addition was also investigated using the NOct$_4$Br/*i*-Bu$_3$Al systems ([Al]/[I] = 1.5−2.0). Results are collected in Table 4.

Table 4. Block Copolymerization of POx with ECH Initiated by $NOct_4Br$ in the Presence of *i*-Bu_3Al (Toluene, Polymerization Time = 1 h for Each Block, T = 20 °C[a], Conversion = 100%, Reinitiation Efficiency >95%)

monomer addition order	[initiator] (mmol/L)	[Al]/[I]	$\bar{M}_n$ (theor) (g/mol) 1st block	2nd block[b]	$\bar{M}_n$ (exp.) (g/mol) diblock	$\bar{M}_w/\bar{M}_n$
POx−ECH	13.0	1.5	5 000	2 000	6 500	1.20
POx−ECH	23.2	1.7	5 000	10 000	12 900	1.33
ECH−POx	15.0	1.7	5 000	10 000	14 700	1.47
ECH−POx	15.0	1.5	5 000	15 000	21 000	1.36
ECH−POx	11.3	2.0	10 000	20 000	29 000	1.29

[a] Initiation was performed at −30 °C and the system allowed to increase. [b] Calculated for a quantitative reinitiation.

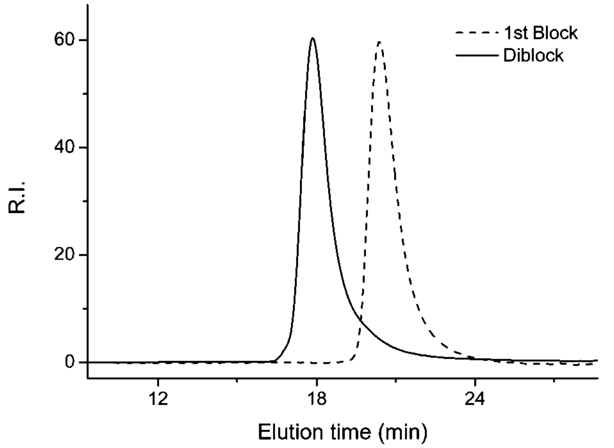


Figure 4. SEC traces corresponding to the different stages of the synthesis of a PECH-*co*-PPOx diblock copolymer ($\bar{M}_n$ = 21 000 g/mol, run 4, Table 4).

Diblock copolymers ranging from about 6 000 g/mol up to 30 000 g/mol with various POx and PECH block lengths were obtained.

The reinitiation efficiency starting either from poly(POx) or poly(ECH) as first block was determined by SEC after quantitative polymerization of the second monomer. As illustrated Figure 4, the SEC trace, corresponding to the first poly(ECH) block, is completely shifted toward higher molar masses in agreement with quantitative formation of a diblock copolymer. Using this approach, poly(POx-*b*-ECH), or in an alternative way poly(ECH-*b*-POx) diblocks, exhibiting experimental molar masses in agreement with theoretical ones and relatively narrow dispersity, were prepared in short reaction times.

Conclusions

The use of triisobutylaluminum in combination with tetraoctylammonium bromide at a stoichiometry $[AlR_3]/[NR_4X] > 1$ appears as an interesting strategy to prepare new anionic-type initiating systems that are able in mild reaction conditions to achieve the living-like polymerization of epichlorohydrin and allow the preparation of well-defined poly(ECH) as well as random and block copolymers of ECH with other epoxide monomers. The Lewis acid additive first reacts with the tetraalkylammonium salt to form a weakly nucleophilic aluminate complex, whereas the excess of AlR_3 acts as a strong activator of the monomer via oxygen−aluminum coordination. In contrast to conventional anionic polymerization, the weakly nucleophilic aluminate species that ensure the propagation are unable to attack the chloromethyl function of ECH and selectively react with the activated epoxide ring allowing preparation of well-defined poly(ECH)-based materials.

Supporting Information Available: ^{13}C NMR spectrum of PECH. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Vandenberg, E. J. *J. Polym. Sci.* **1960**, *47*, 486.
(2) Vairon, J. P.; Spassky, N. In *Cationic Polymerizations; Mechanisms, Synthesis and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker, Inc.: New York, **1996**; Chapter *8*, p 683.
(3) Wolfenson, A. E.; Torresi, R. M.; Bonagamba, T. J.; De Paoli, M. A.; Panepucci, H. *J. Phys. Chem. B* **1997**, *101*, 3469.
(4) Kohjiya, S.; Ikeda, Y. *Mater. Sci. Res. Int.* **1998**, *4*, 73.
(5) Ikeda, Y. *J. Appl. Polym. Sci.* **2000**, *78*, 1530.
(6) Ikeda, Y.; Masui, H.; Matoba, Y. *J. Appl. Polym. Sci.* **2005**, *95*, 178.
(7) Stoica, D.; Ogier, L.; Akrour, L.; Alloin, F.; Fauvarque, J.-F. *Electrochim. Acta* **2007**, *53*, 1596.
(8) Perez, M.; Ronda, J. C.; Reina, J. A.; Serra, A. *Polymer* **2001**, *42*, 1.
(9) Bonet, J.; Callau, L.; Reina, J. A.; Galià, M.; Cádiz, V. *J. Polym. Sci.* **2002**, *40*, 3883.
(10) Frankel, M. B.; Grant, L. R.; Flanagan, J. E. *J. Propul. Power* **1992**, *8*, 560.
(11) Kubota, N.; Yano, Y.; Miyata, K. *Propellants, Explos., Pyrotech.* **1991**, *6*, 287.
(12) Penczek, S. ; Kubisa, P.; Matyjaszewski, K. In *Oxiranes, in Cationic ring opening polymerization part II: synthetic applications. Advances polymer science*; Pepper, D.C., Ed.; Springer Verlag: Berlin, 1985; Vols. *68/69*, Chapter 4, p 52.
(13) Kubisa, P. In *Cationic Polymerizations; Mechanisms, Synthesis and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker, Inc.: New York, **1996**; Chapter 6, p 437.
(14) Penczek, S.; Duda, A.; Kubisa, P.; Slomkowski, S. In *Macromolecular Engineering—Precise Synthesis, Materials Properties, Applications*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: New York, 2007; Vol. *1*, Chapter 4, p 103.
(15) Biedron, T.; Kubisa, P.; Penczek, S. *J. Polym. Sci., Part A* **1991**, *29*, 619.
(16) Vandenberg, E. J. *J. Polym. Sci., Part A: Polym. Chem.* **1969**, *7*, 523.
(17) Araki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1973**, *11*, 699.
(18) Hsieh, H. L. *J. Appl. Polym. Sci.* **1971**, *15*, 2425.
(19) Kuntz, I.; Kroll, W. R. *J. Polym. Sci., Part A: Polym. Chem.* **1970**, *8*, 1601.
(20) Wu, J.; Shen, Z. D. *Polym. J.* **1990**, *22*, 326.
(21) Xie, H.; Guo, J.; Yu, G.; Zu, J. *J. Appl. Polym. Sci.* **2001**, *80*, 2446.
(22) Kuntz, I.; Cozewith, C.; Oakley, H. T.; Via, G.; White, H. G.; Wilchinsky, Z. W. *Macromolecules* **1971**, *4*, 4.
(23) Yagci, Y.; Serhatli, I. E.; Kubisa, P.; Biedron, T. *Macromolecules* **1993**, *26*, 2397.
(24) Royappa, A. T. *J. Appl. Polym. Sci.* **1997**, *65*, 1897.
(25) Kohjiya, S.; Horiuchi, T.; Miura, K.; Kitagawa, M.; Sakashita, T.; Matoba, Y.; Ikeda, Y. *Polym. Int.* **2000**, *49*, 197.
(26) Majid, M. A.; George, M. H.; Barrie, J. A. *Polymer* **1981**, *22*, 1104.
(27) Xie, H.; Pan, S.; Guo, J. *Eur. Polym. J.* **2003**, *39*, 715.
(28) Billouard, C.; Carlotti, S.; Desbois, P.; Deffieux, A. *Macromolecules* **2004**, *37*, 4038.
(29) Rejsek, V.; Sauvanier, D.; Billouard, C.; Desbois, P.; Deffieux, A.; Carlotti, S. *Macromolecules* **2007**, *40*, 6510.
(30) Labbé, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. *Macromolecules* **2007**, *40*, 7842.
(31) Kelen, T.; Tüdos, F. J. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.

MA801422C